

**Research Article**

**Application of biostimulant and CaO to remediate acid mine drainage on the coal mining land in Lampung Sumatra Island**

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**Abstract :** Mining using an open pit system may lead to a deterioration in the quality of the environment in term of the extent of the cleared land, heavy metals contamination on the overburden rock, the formation of acid mine drainage (AMD) with a pH <5, high level of total suspended solid (TSS), and the content of the metal on it. Several research results on post-mining land indicated a change in the environmental quality of the mine. Handling of the AMD problem can be conducted by several methods, including the active method by spreading calcium oxide (CaO) in AMD with the aim of increasing pH to neutral. The purpose of this study was to study the alternative techniques to manage the AMD using biostimulant. The present study was conducted firstly in the vinyl house by using 10 L of AMD water sample with 2 kinds of treatment, i.e. CaO with levels of 0.2 and 0.25. Biostimulant with four kinds of treatment (I, II, III and IV) which resulted from the combination of different types of biostimulants (A, B and C) with different in composition. Secondly, research on the 1000 L of AMD for scaling up applications in the field. CaO and biostimulant doses were obtained from the first stage of the study. Analysis pH, TSS, Fe, and Mn of the AMD were done on the control, CaO, and biostimulant treatments. CaO treatment resulted in an increase in pH to 6.9, TSS decreased significantly decline so to 60 mg/L. Fe content in AMD decreased to 0.22 mg/L, and Mn levels decreased to 0.12 mg/L on day 10. Biostimulant treatment resulted in increase of pH to pH 6.7. The TSS value decreased to 40 mg/L. Fe and Mn levels decreased to 0.03 mg/L and Mn 2.98 mg/L, respectively.

**Keywords:** acid, biostimulant, coal, mine, water

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**Introduction**

Surface mining system may result in environmental degradation due to the extent of open land, overburden rocks containing heavy metals, and the formation of acid mine drainage with a pH <5, as well as the total suspended solid content, and the metal contamination in the soil and water of the offsite area (Dinelli et al., 2001; Akcil and Koldas, 2006). Sulfur in coal and rocks associated with coal mines may occur as organic sulfur, sulfate sulfur, and pyritic sulfur. Some sulfur in coal appears to have been introduced after the peat had been converted to coal, as is

evidenced by pyrite coatings. Many research have been conducted on the post-mining land indicated a change in the environmental quality of the mine land (Sams and Beer, 2000; Akcil and Koldas, 2006; Nurcholis et al., 2013; Simate and Ndlovu, 2014), such as formation of acid mine drainage (AMD). AMD might be formed when certain sulfide minerals in rocks are exposed to oxidizing by mining operation conditions. Metal sulfide Oxidation is the main reason for the formation of sulfuric acid and solubilization of metals (Evangelou, 2001). Addition of an alkaline materials, commonly used, such as CaCO<sub>3</sub> or CaO to AMD will raise its pH, accelerate the rate of

chemical oxidation of ferrous iron (for which active aeration, or addition of a chemical oxidising agent such as hydrogen peroxide, is also necessary), and cause many of the metals present in solution to precipitate as hydroxides and carbonates. In addition, some other metals may also precipitate as hydroxides or carbonates (Johnson and Hallberg, 2005).

Treatment on the acidic water resulting from sulfidic material oxidation might use several methods, such as active treatment (Simate and Ndlovu, 2014) or by spreading calcium oxide (CaO) in acid mine water with the aim of increasing pH to neutral. Active method is conducted by addition of various kinds of alkaline materials that commonly used, such as calcium carbonate ( $\text{CaCO}_3$ ), lime (calcium oxide), slaked lime, sodium carbonate, sodium hydroxide, and magnesium oxide and hydroxide.

Lime (CaO) addition to AMD may increase the pH, accelerating the rate of  $\text{Fe}^{2+}$  oxidation to  $\text{Fe}^{3+}$ , which then precipitates this iron ion. In addition, several other metals may also precipitate as hydroxides or carbonates (Johnson and Hallberg, 2005). This method is commonly done because it is easy to get and very practical use, that is by spreading the limestone to the acid water mine with a certain dose. However, the use of lime is high cost and laborious, and in addition it may lead to sediment on the settling pond. Therefore, the present research was aimed to use passive method in acid mine water treatment, that was using biostimulant and it compared with CaO that was common material for neutralization of acid mine drainage.

Biostimulant is a material that can stimulate the growth of indigenous microbes by adding Nutrients and oxygen in liquid or gaseous form to water or contaminated soil, to strengthen the growth and activity of remediation bacteria already present in the water or soil. Biostimulant application is generally done for the biodegradation process, by providing microbial requirements so that microbes can live and do the biodegradation process. Biostimulant technology is the use of nutrients to trigger microbes to do biodegradation that occurs naturally with biostimulant. The nutrients given in the biostimulant are the triggers of common microbial growth, even the presence of small amounts of contaminants, can be used as a trigger to activate enzymes in microbes. By adding biostimulant materials into the soil or water is the activity of adding nutrients to stimulate the growth of indigenous microbes and microorganisms such as bacteria degrading pollutants (Brown et al., 2003). According to the problem on the formation of acid mine drainage on the coal mining in the research

area, and it may cause environmental deterioration on the on-and off-sites of mining area, indeed there are efforts on the remediation must be done. Application of lime, as  $\text{CaCO}_3$  and or CaO is commonly done to neutralize the AMD, however it is needed huge cost as the price of these materials are high, and also they are produced from limestone mining. It is needed to try alternatives materials that cheaper and environmentally accepted. So that this study was aimed to study the alternative techniques to manage the AMD using biostimulant.

## Materials and Methods

This research was conducted at Pit of coal mining with 16.55 ha of catchment. Runoff water discharge resulted from the coal mining that entering into pit sump was  $1.032 \text{ m}^3/\text{s}$ . The research was conducted in two steps: first step was in plastic house, and the second step was in the field. The first step with a scale of 10 litres of AMD, was intended to obtain and determine an effective dose in neutralizing AMD. The step was done by collecting acid mine drainage sample for 2 kinds of treatment that was: 1) CaO with a dose of 2.0 and 2.5 g/L or 2000 and 2,500 g/1000 L, 2) biostimulant with four kinds of formula with different types of biostimulant (A, B and C) with different composition. Biostimulant I with composition of  $\text{A+B+C} = (150+10+7.5) \text{ g/1000L}$ , Biostimulant II with composition of  $\text{A+B+C} = (150+15+15) \text{ g/1000L}$ , Biostimulant III with composition of  $\text{A+B+C} = (250+20+15) \text{ g/1000L}$ , and Biostimulant IV with composition of  $\text{A+B+C} = (300+30+22.5) \text{ g/1000L}$ .

Biostimulant technology used in this study was the combination of: 1) Biostimulant A containing organic acids, macro elements, micro elements and microorganisms that produces enzymes that degrade the pollutant, by converting the chemical structure into a complex which eventually becomes a harmless metabolite, and serves to neutralize acidic mine water that has pH and metal content not in accordance with water quality standards, by utilizing the bacteria *Thiobacillus ferrooxidans*. organic acid as a food source of the sulphate-degradation bacteria; 2) Biostimulant B organic matter as a food source for microorganisms; 3) Biostimulant C has function of phosphate solubilizing bacteria, degradation bacteria and bacteria decomposers, where the bacteria will develop when contaminated with water and get the nutrients from the water treatment. The experiment was performed with three replications using a completely randomized design to overcome external factors such as light, temperature and

humidity. The analyses of pH, Fe, Mn, and TSS were performed on the control and treated AMD. Optimum dose determination for AMD amelioration was determined using the results of the first step research. The second step of the research was field applications (Figure 1), that it was done after known the effective dose in

neutralizing AMD. In this step, it was used 1000 liters of AMD with the same treatments of CaO and Biostimulant doses from the first research step. Results of the research were analyzed to determine the application of the biostimulant for remediating the AMD in the coal mining area.

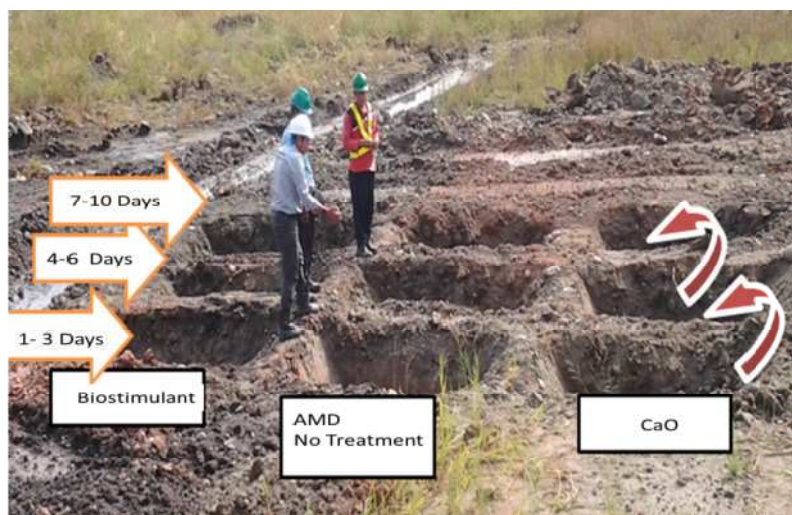


Figure 1. Design of the field research with 1000 L AMD

## Results and Discussion

### *Geography of studied area*

The study area has two morphological units, i.e., the ridge complexes with wavy landform and the alluvial land units. According to the pattern of contours, forms of valleys and river forms, the relative of the two units of morphology clearly looks different. The ridge complexes with wavy landform units are occupying almost 80% of the research areas with altitudes ranging from 60 to 130 meters above sea level. This morphological unit is low altitude hill relief and has a dendritic flow pattern of rivers.

The lithologies of the research area are generally composed of: 1) Top Soil with yellowish gray color, partially separated, fine grained to coarse, well sorted, good porosity.. 2) Quartz Sandstone with whitish yellow, partly loose, fine to coarse grain size, well sorted, rounded to rounded, good porosity, solid, layer thickness up to more than 5 meters. 3) Claystone with gray color, solid. 4) Inserts Shale with colors of gray brownish to blackish, thin-coated, solid, carbonate, coating layer. 5) Carbonaceous claystone blackish gray color, laminate structure, thin-coated, carbonate. 6) Coal seam Inserts with black color, semi concoidal, hardness is dull with a thin coat of glossy coal, little resin, brown

scratches. Coal seam in the area of investigation has a direction or direction N 290 E to 320 E with a slope of 65°- 68°. Hydrologically, the water bodies located in the study area are the three rivers that cross the mining area. The flow patterns of the three rivers are sub-dendritic (occupied by relatively homogeneous lithology and influenced by geological structures), and shows the direction of river flow flowing into the main river. The direction of river flow differs from the direction of the main river flow and has a small catchment area so that the fluctuation of water discharge due to the impact of rainfall is very high. In the dry season, some of the rivers become drought, and in the rainy season, water is excessive. Fluctuations in free groundwater in the study area were between 5m-15m, with groundwater levels varying from 0.05m to 11.4m below the surface. The effect of rainwater on groundwater fluctuations is greater in role than water coming from the horizontal direction, due to the medium permeability.

The cover soil as over burden in the research area is divided into the top layer of top soil and subsoil formed from the weathering of bedrock, consisting of clay, quartz sandstone and sandstone clay. Cap rocks have a moderate to strong degree of weathering, and the average weathering zone reaches a thickness of 5 meters. They consisted of

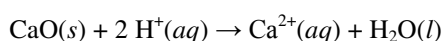
clay, sandstone tuff, and sandstone. Deposition processes of the three layers of this rock ranges from massive or thick to thin, and intermittent. Soil cover and roof rocks include overburden category, i.e. a layer of soil cover that lies between the surfaces with the top layer of coal. Coal seams were generally brownish-black to dull black in colors, and relatively small and thin rocks if compared with others. With the repetition in the deposition process at the study site, the base layer beneath the coal seams has the same type and physical characteristics as the roof layer. The difference lies in the higher density and remains dominated by clay stone units.

Most of the land use is still a forested area of about 70%, consisting of wild forests, protected forests, scrub forests and forests. Approximately 16% is dry land that was is for plantation and grazing land. The area of 12% is a private plantation managed estate. The remaining small part is rice field and settlement land (Table 1). Coal mining activities have the potential to impact on changes in spatial structure of land, especially to land that has been planted. In addition also to the land with shrub vegetation that has been functioning in maintaining water reserves and sources of oxygen for human life.

#### *The first step of research*

##### *Addition of CaO*

The addition of 0.2 and 0.25 g CaO/L dosages increased the pH water from 4.14 to 6.39 and 6.82 respectively (Table 2).



CaO applications of 0.2 and 0.25 g/L decreased TSS levels by 10 days to 5 and 1 mg/L, respectively (Table 3). Biostimulant dosages of I and II were able to decrease TSS levels up to 1

mg/l on the 10th day while dosages of III and IV might decrease to 3 and 2 mg/L, respectively. Initial Fe content of 0.26 mg/L is still far below the standard quality that is set at 7 mg/L. The present study showed that CaO treatment was not very influential in lowering Fe content. CaO doses of 0.2 and 0.25 g/L were able to reduce Fe to 0.18 and 0.21 mg/L on the 10th day. Provision of CaO is more effective in lowering Mn levels compared to Fe content. CaO doses of 0.2 and 0.25 g/L might decrease Mn levels to 0.01 mg/L on the 10th day.

Table 1. Land use in the area around the mine

Land Use Types	Area (ha)	Percent (%)
Paddy fields		
Irrigated paddy field	550	0.6
Rainfed paddy field	377	0.4
Sum	927	1.0
Dry land		
land yard, Building and road	7.879	8.7
Moor/farm land	1.777	2.0
Field	1.655	1.8
Shepherding	3.450	3.8
Sum	14.761	16.4
Forests		
Wilds	13.558	15.1
Shrubs	23.159	25.7
protected forest	6.642	7.4
Production forest	15.085	16.7
Wildlife reserves	4.935	5.5
Sum	63.379	70.4
Plantation	11.000	12.2
Public facilities		
Sport area	2	<0.1
Cemetery	2	<0.1
Total land	90.071	

Table 2. the pH increasing of AMD on the CaO or biostimulants treatment

Treatments	pH value on the days of										
	0	1	2	3	4	5	6	7	8	9	10
Control	4.14	4.38	4.50	4.50	4.39	4.50	4.56	4.53	4.57	4.51	4.50
CaO 2.0g/L	4.14	6.39	6.55	6.55	6.34	6.70	7.03	6.92	6.71	6.62	6.60
CaO 2.5g/L	4.14	6.82	6.95	6.95	6.90	7.08	7.07	7.07	6.85	6.60	6.88
Biostimulant I	4.14	5.21	5.50	5.50	5.90	6.00	6.22	6.24	6.12	6.29	6.43
Biostimulant II	4.14	5.18	5.56	5.56	6.01	6.16	6.24	6.42	6.37	6.30	6.68
Biostimulant III	4.14	5.30	5.60	5.60	6.22	6.22	6.33	6.39	6.42	6.35	6.47
Biostimulant IV	4.14	5.32	5.75	5.75	6.23	6.22	6.40	6.47	6.29	6.32	6.62

From a 10 L of AMD scale tested using CaO with a dose of 2.0 g / 10 Land 2.5 g / 10 L, in increasing pH all doses showed similar increases

but there was a decrease in the dose of 2.0 g / 10 L at the end of the study. At CaO a dose of 2.5 g / 10 L was found to be more effective in decreasing

TSS and Mn levels than 2.0 g / 10 L, and at a dose of 2.0 g / 10 L of Fe more effective in Fe drop than 2.5 g / 10 L. However, Fe levels that are still far below the environmental quality standard will not be the first priority calculated in the selection of CaO doses. pH, TSS, Mn parameters are a priority in determining the experimental dose to be used. Therefore, this study will apply a CaO treatment using a dose of 2.5 g / 10 L.

#### *Addition of biostimulant*

Trial application with 10 litres of AMD used 4 doses of experiment. Just like the application of CaO scale 10 litres of AMD, the application using biostimulant also used randomized design pattern with the result. Biostimulant with composition formula of I, II or III, was able to increase water pH reached standard quality on 4<sup>th</sup> day, that was pH 6.01, 6.22, 6.23, respectively (Table 2). Initial TSS level of 183 mg/L was able to be decreased by all treatments. Result of the experiment showed that biostimulant applications were able to neutralize pH to reach standard quality on day 4 for dose of II, III and IV, but for dose of I got a same result at day 5 (Table 2). The biostimulant contains macro elements (N, P, K, Ca, S, Mg),

micro elements (Cl, Mn, Fe, Cu, Zn, Pb, Br, etc.), and microbes (N fixation, phosphate solubilizers, decomposers), growth stimulants (auxin, cytokines, gibberellins). In this case, biostimulant has functions such as neutralize pH, absorbing heavy metals such as Fe, Mn, etc., and environmentally friendly. TSS levels for each dose of biostimulant used decreased. Significant decrease at the end of the study or at day 10 occurred at doses of I and II of 1 mg/L. As for the doses of III and IV there is an increase in TSS levels to 3 mg/L and 2 mg/L. It was due to the number of biostimulant products used in Doses III and IV. Therefore, biostimulant at doses of I and II may be better used in lowering TSS. The use of biostimulant relates to the flocculation of small particles to be bigger size particles. The flocs generated in natural systems possess a multilevel structure (Chu et al, 2002). The activated biosolids floc formation model of Gorczyca and Ganczaeczyk (1999) involves primary particles with diameter of 1–2 mm, flocculi with diameter of 5–10 mm, microflocs with diameter of several tens mm, and whole flocs with diameter of 100–200 mm (Chu et al., 2002).

Table 3. Values of TSS, Fe, and Mn of AMD after CaO or biostimulants application

Treatment	TSS on the days of					Fe on the days of			Mn on the days of		
	0	1	4	7	10	0	1	10	0	1	10
	-----mg/L-----										
Control	183	10	5	2	1	0.26	0.26	0.25	4.18	4.18	3.52
CaO 2.0 g/L	183	55	7	4	2	0.26	0.26	0.18	4.18	4.18	0.01
CaO 2.5 g/L	183	40	6	4	5	0.26	0.26	0.21	4.18	4.18	0.01
Biostimulant I	183	41	4	1	1	0.26	0.26	0.06	4.18	4.18	3.30
Biostimulant II	183	38	5	2	1	0.26	0.26	0.06	4.18	4.18	2.79
Biostimulant III	183	39	5	1	3	0.26	0.26	0.05	4.18	4.18	3.35
Biostimulant IV	183	45	6	3	2	0.26	0.26	0.07	4.18	4.18	3.35

The most effective dose of biostimulant in Fe content decrease was at the III formula of 0.05 mg/L, while for Mn metals the more effective dose in Mn drop was II formula of 2.79 mg/L (Table 3). Mn level before treatment was still above the standard quality of 4.18 mg/L. In the biostimulant compositions II, III and IV decreased Fe content of 0.06, 0.05 and 0.07 mg/L, respectively on the 10th day. According to the results, it can be stated that biostimulant was slightly slow in decreasing Mn levels. Biostimulant compositions of I, II, III and IV were able to decrease Mn levels to 3.30, 2.97, 3.35, and 3.35 on the 10th day. From the above results, it can be seen that the Fe content is still far below the quality standard set so it is not a top

priority in determining the dose of experiment to be in use. The main priority is in reducing the amount of Mn metal in acid mine water that is studied because it is still above the standard quality that is set, that is 4.18 mg/L. So the recommended dose is the II formula biostimulant because it can be more effective in reducing Mn level to 2.79 mg/L.

#### *The second step of research*

Based on the results obtained from the experimental scale of 10 litres, then it was followed by the field treatment at the scale of 1000 liter of AMD by using CaO level of 2.5 g/10 L or 2500 g/1000 L, and biostimulant treatment was using composition II.

### The pH of water

The use of CaO ameliorant might increase the pH of water on the first day until 7.89, however it was little decrease until pH 6.9 on the tenth day. The biostimulant was able to increase the pH of water to reach the water quality standard on day 3 that is pH 6.2 and continue to rise until pH 6.7 on day

10. The results of the treatment using CaO and biostimulants were analyzed on day 10. The pH value of mine acid treatment in all CaO treatment showed an increase. On treatment of oxidized lime (CaO) The significant increase of pH occurred on the first day of 7.89 with effectiveness of increase of 47.52% but on day 9 the pH decreased to pH 6.9 (Figure 2).

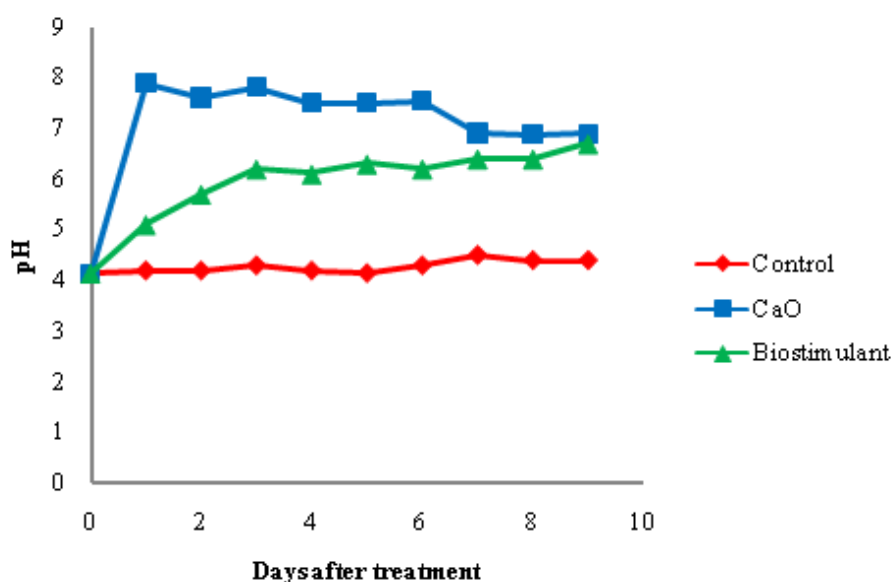


Figure 2. The pH value of the AMD after CaO and biostimulant application

CaO and biostimulant application treatment resulted in the increase of pH reached the quality standard achieved on the 4th day that is pH 6.2 (Figure 2). But unlike the CaO treatments, on the 9<sup>th</sup> day the biostimulant treatments continued to increase in pH to 6.7. That is because biostimulant is a nutrient for the development of microorganisms in neutralizing acid water mine so that it will continue to proceed without any provision of treatments again. Therefore, it is necessary to design a compartment to accommodate AMD for treatment using biostimulant can proceed well. Addition of biosolids alone on tailings resulted in a significant but smaller increase in pore water pH when compared to lime, that was 1–2 pH units versus 4–5 units, respectively (Verdugo et al., 2010)

### Total Suspended Solids (TSS)

Initial TSS levels were 320 mg/Liter, the use of CaO treatment decreased levels to 60 mg/L, whereas biostimulants decreased levels to 40 mg/L. The initial TSS in the AB Pit sump water that flowed into the experimental pool was 320 mg/L. After treatment of the research conducted

in each test pool, then the water quality analysis, and obtained results as in. the highest TSS levels in the 10th day on AMD without treatment. For the lowest level of TSS was achieved on 10th day after treatment of CaO 60 mg/L, while for biostimulant that was in the 40 mg/ (Figure 3).

### Iron (Fe) content on the AMD

The initial Fe content before ameliorant addition was 0.26 mg/L. The CaO application did not decrease significant Fe content, which only reached 0.22 mg/L, while for biostimulant can decrease Fe content up to 0.03 mg/L. There was a difference between the treatment using biostimulant comparing to the lime treatment and control. It is because the sulfides produced by the sulfate reducing bacteria react with dissolved metal ions to form sulfide metal deposited for example iron sulfide (FeS) (Figure 4).

### Manganese (Mn) content on the AMD

The initial Mn level is still above the water quality standard of 4.18 mg/L. The treatment of CaO was very effective in lowering Mn levels up to 0.12 mg/L, whereas for biostimulants it only decreased

to 2.98 mg/L. Mn initial rate before treatment was 4.18 mg/L. the most significant decrease occurred in the processing using oxidized lime on the analysis day 9, which is 0.12 mg/L (Figure 5). This is because lime can raise the pH quickly so that the decrease in Mn can run optimally. While for biostimulant on day 9 reached 2.98 mg/L with. This is due to the presence of micro elements of

Mn content in biostimulants as well as the nature of the initial Mn dissolves and only quickly settles at a pH above 7. While for biostimulant on day 9 reached 2.98 mg/L with. This is because of the micro element of Mn content in biostimulant and Mn properties are easily soluble and only quickly settles at pH above 7.

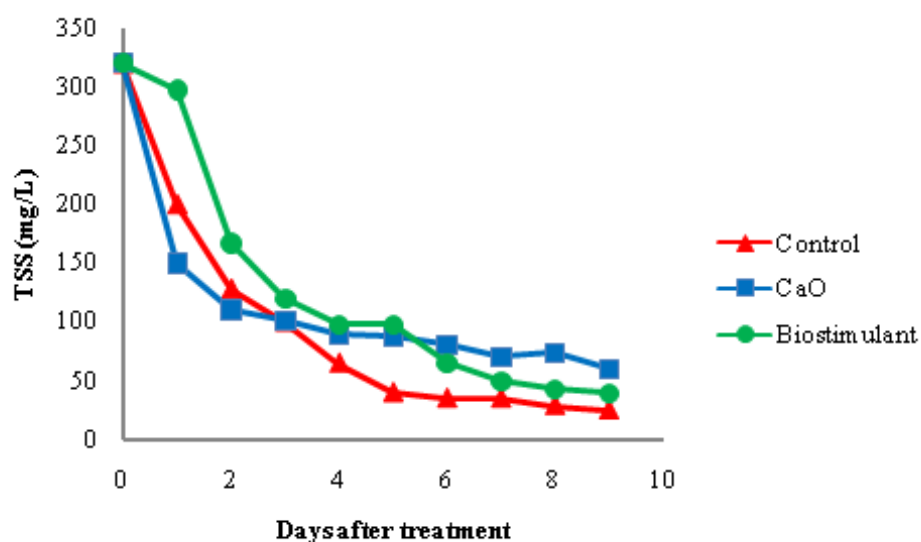


Figure 3. The TSS value of the AMD after CaO and biostimulant application

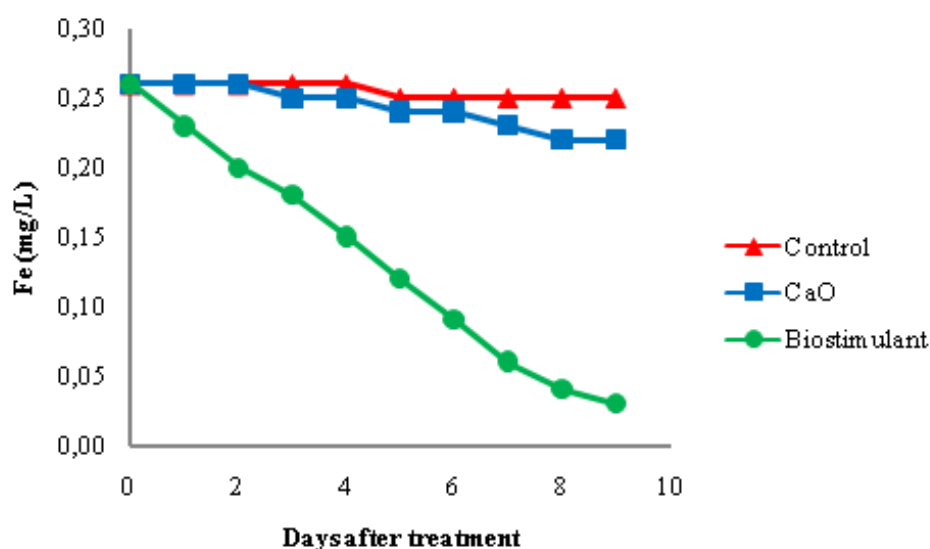


Figure 4. The Fe content of the AMD after CaO and biostimulant



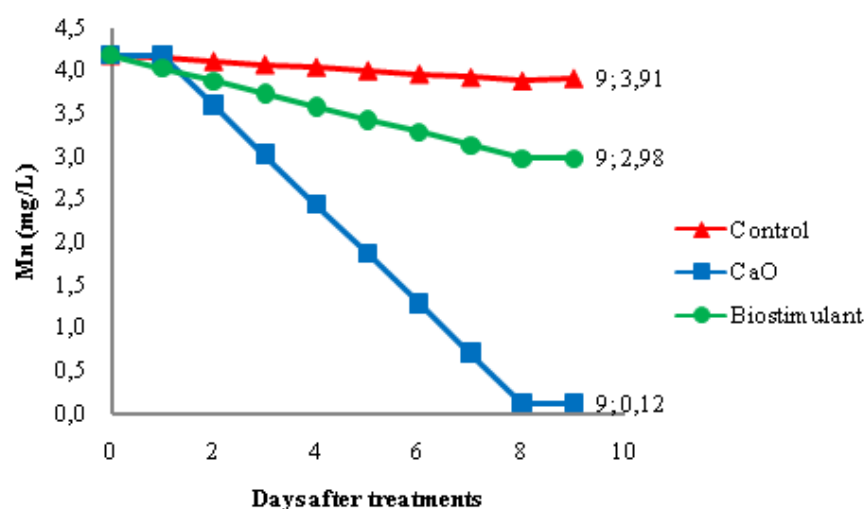


Figure 5. The Mn content of the AMD after CaO and biostimulant application

## Conclusions

CaO treatment resulted in an increase in pH to reach the standard on the first day of pH 7.89 but on day 10 there was a decrease in pH of 6.9. TSS decreased significantly on the first day to 150 mg/L and continued to decline so that on day 10 to 60 mg/L. Fe content in AMD decreased to 0.22 mg/L. Mn levels decreased to 0.12 mg/L on day 10. The use of the Biostimulant Treatment resulted in a decrease in pH to reach the standard on day 4 of pH 6.2 and continued to increase in neutral reach of pH 6.7 on day 10. The TSS value decreased to 297 mg/L on day one, and as time goes on down to the 10<sup>th</sup> day of significant decrease to 40 mg/L. Fe and Mn levels experienced decreased samples on the 10<sup>th</sup> day to 0.03 mg/L and Mn 2.98 mg/L.

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